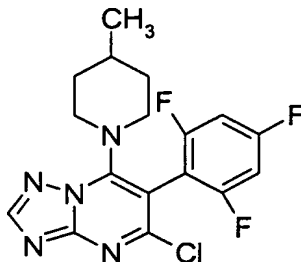


Fungicidal mixtures

The present invention relates to fungicidal mixtures comprising, as active components,

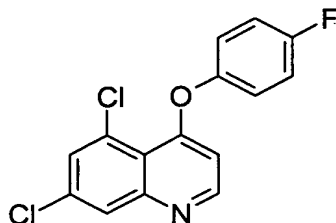
- 5 1) the triazolopyrimidine derivative of the formula I



I

and

- 2) quinoxifen of the formula II



II

10

in a synergistically effective amount.

Moreover, the invention relates to a method for controlling harmful fungi from the class of the Oomycetes using mixtures of the compound I with the compound II, to the use of
15 the compound I with the compound II for preparing such mixtures and to compositions comprising these mixtures.

The compound I, 5-chloro-7-(4-methylpiperidin-1-yl)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, its preparation and its action against harmful fungi are known
20 from the literature (WO 98/46607).

The compound II, 5,7-dichloro-4-(4-fluorophenoxy)quinoline, its preparation und its action against harmful fungi are also known from the literature (US 5 240 940; common name: quinoxifen). Quinoxifen has been commercially established as a fungicide
25 against mildew diseases.

Mixtures of triazolopyrimidine derivatives with quinoxifen are known in a general manner from EP-A 988 790. The compound I is embraced by the general disclosure of this publication, but not explicitly mentioned. Accordingly, the combination of compound I
30 with quinoxifen is novel.

Nr

The synergistic mixtures of triazolopyrimidines described in EP-A 988 790 are described as being fungicidally active against various diseases of cereals, fruit and vegetables, in particular mildew on wheat and barley or gray mold on apples. However,
5 the fungicidal action of these mixtures against harmful fungi from the class of the *Oomycetes* is unsatisfactory.

The biological behavior of *Oomycetes* is clearly different from that of the *Ascomycetes*, *Deuteromycetes* and *Basidiomycetes*, since *Oomycetes* are biologically more closely
10 related to algae than to fungi. Accordingly, what is known about the fungicidal activity of active compounds against "true fungi" such as *Ascomycetes*, *Deuteromycetes* and *Basidiomycetes* can be applied only to a very limited extent to *Oomycetes*.

Oomycetes cause economically relevant damage to various crop plants. In many
15 regions, infections by *Phytophthora infestans* in the cultivation of potatoes and tomatoes are the most important plant diseases. In viticulture, considerable damage is caused by peronospora of grapevines.

There is a constant demand for novel compositions against *Oomycetes* in agriculture,
20 since there is already widespread resistance of the harmful fungi to the products established in the market, such as, for example, metalaxyl and active compounds of a similar structure.

Practical agricultural experience has shown that the repeated and exclusive application
25 of an individual active compound in the control of harmful fungi leads in many cases to a rapid selection of such fungus strains which have developed natural or adapted resistance against the active compound in question. Effective control of these fungi with the active compound in question is then no longer possible.

To reduce the risk of selection of resistant fungus strains, mixtures of different active
30 compounds are nowadays preferably employed for controlling harmful fungi. By combining active compounds having different mechanisms of action, it is possible to ensure a successful control over a relatively long period of time.

It is an object of the present invention to provide, with a view to effective resistance
35 management and an effective control of harmful fungi from the class of the *Oomycetes* at application rates which are as low as possible, mixtures which, at a reduced total amount of active compounds applied, have a satisfactory effect against the harmful
40 fungi.

We have found that this object is achieved by the mixtures defined at the outset. Moreover, we have found that simultaneous, that is joint or separate, application of the compound I and the compound II or successive application of the compounds I and the compound II allows better control of *Oomycetes* than is possible with the individual compounds (synergistic mixtures).

The mixtures of the compound I and the compound II or the simultaneous, that is joint or separate, use of the compound I and the compound II are distinguished by being very highly active against phytopathogenic fungi from the class of the *Oomycetes*, in particular of *Phytophthora infestans* on potatoes and tomatoes and *Plasmopara viticola* on grapevines. They can be used in crop protection as foliar- and soil-acting fungicides.

They are particularly important for controlling *Oomycetes* on various crop plants such as vegetable plants (for example cucumbers, lettuce and cucurbits), potatoes, tomatoes, grapevines and the corresponding seeds.

They are particularly suitable for controlling late blight on tomatoes and potatoes caused by *Phytophthora infestans* and downy mildew of grapevines (peronospora of grapevines) caused by *Plasmopara viticola*.

In addition, the combination according to the invention of the compounds I and II is also suitable for controlling other pathogens such as, for example, *Septoria* and *Puccinia* species in cereals and *Alternaria* and *Botrytis* species in vegetables, fruit and grapevines.

When preparing the mixtures, it is preferred to employ the pure active compounds I and II, to which further active compounds against harmful fungi or against other pests, such as insects, arachnids or nematodes, or else herbicidal or growth-regulating active compounds or fertilizers can be added according to need.

Further suitable active compounds in the above sense are, in particular, fungicides selected from the following group:

- acylalanines, such as benalaxyl, metalaxyl, ofurace or oxadixyl,
- amine derivatives, such as aldimorph, dodemorph, fenpropidin, guazatine, iminotadine or tridemorph,
- antibiotics, such as cycloheximide, griseofulvin, kasugamycin, natamycin, polyoxin or streptomycin,
- azoles, such as bitertanol, bromoconazole, cyproconazole, difenoconazole, dinitroconazole, enilconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hex-

- aconazole, imazalil, ipconazole, myclobutanil, penconazole, propiconazole, prochloraz, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triflumizole or triticonazole,
- dicarboximides, such as myclozolin or procymidone,
 - 5 • dithiocarbamates, such as ferbam, nabam, metam, propineb, polycarbamate, ziram or zineb,
 - heterocyclic compounds, such as anilazine, boscalid, carbendazim, carboxin, oxy-carboxin, cyazofamid, dazomet, famoxadone, fenamidone, fuberidazole, flutolanil, furametpyr, isoprothiolane, mepronil, nuarimol, probenazole, pyroquilon, silthiofam,
 - 10 • thiabendazole, thifluzamide, tiadinil, tricyclazole or triforine,
 - nitrophenyl derivatives, such as binapacryl, dinocap, dinobuton or nitrophthal-isopropyl,
 - phenylpyrroles, such as fenpiclonil or fludioxonil,
 - sulfur,
 - 15 • other fungicides, such as acibenzolar-S-methyl, carpropamid, chlorothalonil, cyflufenamid, cymoxanil, diclomezine, diclocymet, diethofencarb, edifenphos, ethaboxam, fenhexamid, fentin acetate, fenoxanil, ferimzone, fluazinam, fosetyl, hexachlorobenzene, metrafenone, pencycuron, propamocarb, phthalide, toloclofos-methyl, quintozone or zoxamide,
 - 20 • strobilurins, such as fluoxastrobin, metominostrobin, oryastrobin, pyraclostrobin or trifloxystrobin,
 - sulfenic acid derivatives, such as captafol,
 - cinnamides and analogous compounds, such as flumetover.
- 25 In one embodiment of the mixtures according to the invention, the compounds I and II are admixed with a further fungicide III or two fungicides III and IV. Preference is given to mixtures of the compounds I and II with a component III. Particular preference is given to mixtures of the compounds I and II.
- 30 The compound I and the compound II can be applied simultaneously, that is jointly or separately, or in succession, the sequence, in the case of separate application, generally not having any effect on the result of the control measures.
- In the control of phytopathogenic harmful fungi, the separate or joint application of the
- 35 compound I and the compound II or of the mixtures of the compound I and the compound II is carried out by spraying or dusting the seeds, the plants or the soils before or after sowing of the plants or before or after emergence of the plants. The mixtures are preferably applied by spraying the leaves.

The compound I and the compound II are usually applied in a weight ratio of from 100:1 to 1:100, preferably from 50:1 to 1:10, in particular from 10:1 to 1:5.

- 5 The components III and, if appropriate, IV are, if desired, added in a ratio of from 20:1 to 1:20 to the compound I.

Depending on the type of compound and the desired effect, the application rates of the mixtures according to the invention are from 5 g/ha to 2000 g/ha, preferably from 50 to 1500 g/ha, in particular from 50 to 750 g/ha.

Correspondingly, the application rates for the compound I are generally from 1 to 1000 g/ha, preferably from 10 to 750 g/ha, in particular from 20 to 500 g/ha.

- 15 Correspondingly, the application rates for the compound II are generally from 5 to 2000 g/ha, preferably from 10 to 1000 g/ha, in particular from 50 to 750 g/ha.

In the treatment of seed, application rates of mixture are generally from 1 to 1000 g/100 kg of seed, preferably from 1 to 750 g/100 kg, in particular from 5 to 500 g/100 kg.

The mixtures according to the invention, or the compounds I and II, can be converted into the customary formulations, for example solutions, emulsions, suspensions, dusts, powders, pastes and granules. The use form depends on the particular intended purpose; in each case, it should ensure a fine and even distribution of the compound according to the invention.

The formulations are prepared in a known manner, for example by extending the active compound with solvents and/or carriers, if desired using emulsifiers and dispersants.

30 Solvents/auxiliaries suitable for this purpose are essentially:

- water, aromatic solvents (for example Solvesso products, xylene), paraffins (for example mineral oil fractions), alcohols (for example methanol, butanol, pentanol, benzyl alcohol), ketones (for example cyclohexanone, gamma-butyrolactone), pyrrolidones (NMP, NOP), acetates (glycol diacetate), glycols, fatty acid dimethylamides, fatty acids and fatty acid esters. In principle, solvent mixtures may also be used,
- carriers such as ground natural minerals (for example kaolins, clays, talc, chalk) and ground synthetic minerals (for example highly disperse silica, silicates); emulsifiers such as nonionic and anionic emulsifiers (for example polyoxyethylene fatty alcohol

ethers, alkylsulfonates and arylsulfonates) and dispersants such as lignin-sulfite waste liquors and methylcellulose.

Suitable surfactants used are alkali metal, alkaline earth metal and ammonium salts of
5 lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid,
dibutyl naphthalenesulfonic acid, alkylarylsulfonates, alkyl sulfates, alkylsulfonates, fatty
alcohol sulfates, fatty acids and sulfated fatty alcohol glycol ethers, furthermore
condensates of sulfonated naphthalene and naphthalene derivatives with
10 formaldehyde, condensates of naphthalene or of naphthalenesulfonic acid with phenol
and formaldehyde, polyoxyethylene octylphenyl ether, ethoxylated isooctylphenol,
octylphenol, nonylphenol, alkylphenyl polyglycol ethers, tributylphenyl polyglycol ether,
tristearylphenyl polyglycol ether, alkylaryl polyether alcohols, alcohol and fatty alcohol
ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers,
15 ethoxylated polyoxypropylene, lauryl alcohol polyglycol ether acetal, sorbitol esters,
lignosulfite waste liquors and methylcellulose.

Substances which are suitable for the preparation of directly sprayable solutions,
emulsions, pastes or oil dispersions are mineral oil fractions of medium to high boiling
point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or
20 animal origin, aliphatic, cyclic and aromatic hydrocarbons, for example toluene, xylene,
paraffin, tetrahydronaphthalene, alkylated naphthalenes or their derivatives, methanol,
ethanol, propanol, butanol, cyclohexanol, cyclohexanone, isophorone, highly polar
solvents, for example dimethyl sulfoxide, N-methylpyrrolidone or water.

25 Powders, materials for spreading and dustable products can be prepared by mixing or
concomitantly grinding the active substances with a solid carrier.

Granules, for example coated granules, impregnated granules and homogeneous
granules, can be prepared by binding the active compounds to solid carriers. Examples
30 of solid carriers are mineral earths such as silica gels, silicates, talc, kaolin, attaclay,
limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate,
magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, such as,
for example, ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and
products of vegetable origin, such as cereal meal, tree bark meal, wood meal and
35 nutshell meal, cellulose powders and other solid carriers.

In general, the formulations comprise from 0.01 to 95% by weight, preferably from 0.1
to 90% by weight, of the active compounds. In this case, the active compounds are
employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR
40 spectrum).

The following are examples of formulations: 1. Products for dilution with water

5

A) Water-soluble concentrates (SL)

10 parts by weight of the active compounds are dissolved in water or in a water-soluble solvent. As an alternative, wetters or other auxiliaries are added. The active compound dissolves upon dilution with water.

10

B) Dispersible concentrates (DC)

20 parts by weight of the active compounds are dissolved in cyclohexanone with addition of a dispersant, for example polyvinylpyrrolidone. Dilution with water gives a dispersion.

15

C) Emulsifiable concentrates (EC)

15 parts by weight of the active compounds are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5% strength). Dilution with water gives an emulsion.

20

D) Emulsions (EW, EO)

40 parts by weight of the active compounds are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5% strength). This mixture is introduced into water by means of an emulsifier machine (Ultraturrax) and made into a homogeneous emulsion. Dilution with water gives an emulsion.

25

E) Suspensions (SC, OD)

In an agitated ball mill, 20 parts by weight of the active compounds are comminuted with addition of dispersants, wetters and water or an organic solvent to give a fine active compound suspension. Dilution with water gives a stable suspension of the active compound.

30

F) Water-dispersible granules and water-soluble granules (WG, SG)

50 parts by weight of the active compounds are ground finely with addition of dispersants and wetters and made as water-dispersible or water-soluble granules by means of technical appliances (for example extrusion, spray tower, fluidized bed). Dilution with water gives a stable dispersion or solution of the active compound.

35

G) Water-dispersible powders and water-soluble powders (WP, SP)

75 parts by weight of the active compounds are ground in a rotor-stator mill with addition of dispersants, wetters and silica gel. Dilution with water gives a stable dispersion or solution of the active compound.

5 2. Products to be applied undiluted

H) Dustable powders (DP)

5 parts by weight of the active compounds are ground finely and mixed intimately with 95% of finely divided kaolin. This gives a dustable product.

10

I) Granules (GR, FG, GG, MG)

0.5 part by weight of the active compounds is ground finely and associated with 95.5% carriers. Current methods are extrusion, spray-drying or the fluidized bed. This gives granules to be applied undiluted.

15

J) ULV solutions (UL)

10 parts by weight of the active compounds are dissolved in an organic solvent, for example xylene. This gives a product to be applied undiluted.

20 The active compounds can be used as such, in the form of their formulations or the use forms prepared therefrom, for example in the form of directly sprayable solutions, powders, suspensions or dispersions, emulsions, oil dispersions, pastes, dustable products, materials for spreading, or granules, by means of spraying, atomizing, dusting, spreading or pouring. The use forms depend entirely on the intended
25 purposes; they are intended to ensure in each case the finest possible distribution of the active compounds according to the invention.

Aqueous use forms can be prepared from emulsion concentrates, pastes or wettable
30 powders (sprayable powders, oil dispersions) by adding water. To prepare emulsions, pastes or oil dispersions, the substances, as such or dissolved in an oil or solvent, can be homogenized in water by means of a wetter, tackifier, dispersant or emulsifier. However, it is also possible to prepare concentrates composed of active substance, wetter, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil, and such concentrates are suitable for dilution with water.

35

The active compound concentrations in the ready-to-use preparations can be varied within relatively wide ranges. In general, they are from 0.0001 to 10%, preferably from 0.01 to 1%.

The active compounds may also be used successfully in the ultra-low-volume process (ULV), it being possible to apply formulations comprising over 95% by weight of active compound, or even to apply the active compound without additives.

- 5 Oils of various types, wetters, adjuvants, herbicides, fungicides, other pesticides, or bactericides may be added to the active compounds, even, if appropriate, just immediately prior to use (tank mix). These agents can be admixed with the compositions according to the invention, usually done in a weight ratio from 1:10 to 10:1.

10

The compounds I and II, the mixtures or the corresponding formulations are applied by treating the harmful fungi, the plants, seeds, soils, areas, materials or spaces to be kept free from them with a fungicidally effective amount of the mixture or, in the case of separate application, of the compounds I and II. Application can be carried out before or after infection by the harmful fungi.

15

The fungicidal action of the compound and of the mixtures can be demonstrated by the following experiments:

- 20 The active compounds, separately or jointly, were prepared as a stock solution comprising 0.25% by weight of active compound in acetone or DMSO. 1% by weight of the emulsifier Uniperol® EL (wetting agent having emulsifying and dispersant action based on ethoxylated alkylphenols) was added to this solution, and the mixture was diluted with water to the desired concentration.

25

Use example – activity against peronospora of grapevines caused by *Plasmopara viticola*

- 30 Leaves of potted vines of the cultivar "Riesling" were sprayed to runoff point with an aqueous suspension having the concentration of active compound stated below. The next day, the undersides of the leaves were inoculated with an aqueous zoospore suspension of *Plasmopara viticola*. The grapevines were then initially placed in a water-vapor-saturated chamber at 24°C for 48 hours and then in a greenhouse at 20-30°C for 5 days. After this period of time, the plants were again placed in a humid chamber for 16 hours to promote sporangiophore eruption. The extent of the development of the disease on the undersides of the leaves was then determined visually.

35

- 40 The visually determined percentages of infected leaf areas were converted into efficacies in % of the untreated control:

The efficacy (E) is calculated as follows using Abbot's formula:

$$E = (1 - \alpha/\beta) \cdot 100$$

5

- α corresponds to the fungicidal infection of the treated plants in % and
 β corresponds to the fungicidal infection of the untreated (control) plants in %

10

An efficacy of 0 means that the infection level of the treated plants corresponds to that of the untreated control plants; an efficacy of 100 means that the treated plants were not infected.

15

The expected efficacies of combinations of active compounds were determined using Colby's formula (Colby, S.R. "Calculating synergistic and antagonistic responses of herbicide combinations", Weeds, 15, pp. 20-22, 1967) and compared with the observed efficacies.

Colby's formula:

20

$$E = x + y - x \cdot y / 100$$

E expected efficacy, expressed in % of the untreated control, when using the mixture of the active compounds A and B at the concentrations a and b

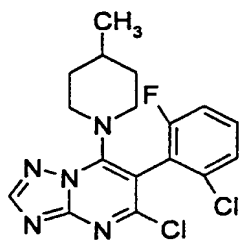
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x efficacy, expressed in % of the untreated control, when using the active compound A at the concentration a

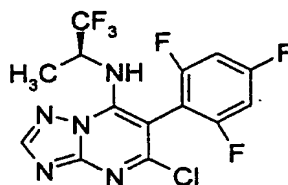
y efficacy, expressed in % of the untreated control, when using the active compound B at the concentration b

30

The comparative compounds used were compounds A and B which are known from the quinoxifen mixtures described in EP-A 988 790:



A



B

Table A – Individual active compounds

Ex-ample	Active compound	Concentration of active compound in the spray liquor [ppm]	Efficacy in % of the untreated control
1	-	control (untreated)	(84% infection)
2	I	4	52
3	II (quinoxifen)	16	16
		1	0
4	comparative compound A	4	16
5	comparative compound B	4	52

Table B – Mixtures according to the invention

Ex-ample	Mixture of active compounds Concentration Mixing ratio	Observed efficacy	Calculated efficacy*)
6	I+II	76	52
	4+1 ppm 4:1		
7	I+II	82	60
	4+16 ppm 1:4		

5 *) efficacy calculated using Colby's formula

Table C – Comparative tests – mixtures known from EP-A 988 780

Ex-ample	Mixture of active compounds Concentration Mixing ratio	Observed efficacy	Calculated efficacy*)
8	A + II 4 + 1 ppm 4:1	28	16
9	A + II 4 + 16 pm 1:4	28	16
10	B + II 4 + 1 ppm 4:1	52	52
11	B + II 4 + 16 pm 1:4	52	52

*) efficacy calculated using Colby's formula

5 The test results show that, by virtue of strong synergism, the mixtures according to the invention are considerably more effective against peronospora of grapevines than the quinoxifen mixtures known from EP-A 988 780.